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CANADIAN PATENT

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ARTICLES EXHIBITING ANTIMICROBIAL PROPERTIES

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The present invention relates to articles fabricated from polymeric materials which are resistant to the growth of microorganisms. In one aspect, the invention relates to a method of inhibiting the growth of microorganisms in or on polymeric materials. In another aspect, the invention relates to bactericidal surfaces.

Bacteriocides, germicides and antimicrobial compositions are well known in the art. Organic quaternary ammonium salts, organic tin compounds and phenolic derivatives are commonly used to kill or control the growth of non-filterable microorganisms, such as bacteria, fungi and algae. Certain organosilicon amines are known to be toxic and have alleged utility as fungicides, insecticides and the like as disclosed in Belgian Patent No. 789,399 dated March 28, 1973, and U.S. Patent No. 2,930,809 which states that "...the dialkoxymethylsilylbutylamines, unlike their homologs referred to above, are extremely poisonous and find wide utility in the preparation of pesticides, fungicides...." The salts of certain organosilicon amines have also been described as fungicides and bactericides - see Maki et al., Yukagku 19 (11), Nov. 1970, 1029-33; CA 74 (8), 32907 V. which shows the hydrochloride salt of tributylsilylpropyldimethylamine to be active against S. aureus 209 P and E. coli B. and Canadian Patent No. 774,529 which refers to organosilicon quaternary ammonium halides at page 3 as "bactericides and fungicides".

The prior art does not disclose a suitable method for utilizing the organosilicon compounds to provide antimicrobial properties in plastic and elastomeric materials. Merely incorporating the appropriate organosilicon amine or amine salt in an uncured plastic material is not entirely satisfactory because one must use an excess of the amine to ensure that the



amine "bleeds" to the surface and the use of an excess can adversely affect the physical properties of the material and result in an ecologically undesirable release of the amine into the environment.

By the practice of the present invention wherein an organosilicon treated filler is incorporated in a polymeric matrix, plastic and elastomeric materials which exhibit enhanced anti-microbial activity that cannot be diminished by extraction or leaching are provided.

10 Thus, it is an object of the present invention to provide polymeric composites which are resistant to the growth of nonfilterable microorganisms.

It is another object of the present invention to provide a method of inhibiting the growth of bacteria, fungi and algae in or on polymeric materials.

Still another object of the present invention is to provide polymeric materials having the capability of controlling or reducing bacterial activity.

20 These and other objects will become apparent to one skilled in the art upon consideration of the following specification and claims.

In accordance with the present invention, there is provided an article comprising a filled polymeric matrix containing a solid filler which has coated on the surface thereof an organosilicon compound selected from the group consisting of polymers of the unit formula $X^{\ominus}R_3N^{\oplus}R'SiO_{3-a}$ $\begin{matrix} \downarrow \\ Y_a \end{matrix}$ $\frac{2}{2}$

and polymers of the unit formula $X^{\ominus}\text{C}_6\text{H}_4\text{N}^{\oplus}R'SiO_{3-a}$ $\begin{matrix} \downarrow \\ Y_a \end{matrix}$ $\frac{2}{2}$ in which

30 X is an acid anion; R is a monovalent hydrocarbon radical

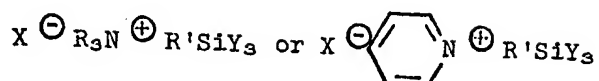
containing from 1 to 20 inclusive carbon atoms, R' is a divalent hydrocarbon radical containing no more than 20 carbon atoms or a substituted divalent hydrocarbon radical of no more than 20 carbon atoms containing oxygen in the form of -COC- , $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{OC-}$, $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}$

or $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{OH}$ groups or nitrogen in the form of R"N- groups in which R" is a hydrogen atom or a lower alkyl radical; Y is a hydroxyl group or a hydrolyzable radical; and a has a value of 0 or 1; the organosilicon coating being present in an amount sufficient to
 10 inhibit the growth of fungi, bacteria or algae in or on the polymeric matrix.

The above-described article is protected against attack by microorganisms. The antimicrobial activity imparted by the organosilicon quaternary ammonium salt is bonded to a solid and does not bloom or leach from the polymer. Because of the bonding, there is no transfer to or contamination of other articles which may come into contact with the polymeric material and there can be no undesirable release of the active chemical into the surrounding environment. Surface abrasion of the article does
 20 not provide opportunity for attack by microorganisms since the coated filler is dispersed throughout the polymeric matrix. In addition to providing for preservation of the article, the antimicrobial activity is available to kill microorganisms brought into contact with the polymeric material. Thus, one could reduce the bacterial count of water by passing it through a filter packed with synthetic fibers which have the treated filler incorporated therein.

The organosilicon quaternary salts used to coat the solid fillers can be either silanes or siloxanes in the form
 30 of partial condensates of silane monomers. The silanes are

of the general formula



in which X, R, R' and Y are as defined. Since the Y groups hydrolyze in the presence of moisture at room temperature, the active species are the corresponding silanols or partial condensates (siloxane) which is coated onto the surface of the solid filler. Partial condensates are those siloxanes which contain at least one hydroxyl or hydrolyzable radical condensation of the silanols gives the $X^{\ominus}R_3N^{\oplus}R'SiO_{3/2}$, $X^{\ominus}\text{C}_6\text{H}_4N^{\oplus}R'SiO_{3/2}$, $X^{\ominus}R_3N^{\oplus}R'SiO_{2/2}$ and/or $X^{\ominus}\text{C}_6\text{H}_4N^{\oplus}R'SiO_{2/2}$ coatings

specified in the present invention.

The organosilicon quaternary ammonium salts are well-known materials and are described in numerous publications and patents. One convenient method of preparing the salts is to react a halohydrocarbon-functional silane with a tertiary amine; i.e., $\equiv\text{SiR}'\text{X} + \text{R}_3\text{N} \longrightarrow \equiv\text{SiR}'\text{N}^{\ominus}\text{R}_3\text{X}^{\oplus}$. If desired, excess halohydrocarbon silane can be used to insure complete reaction of the amine. The quaternary salts can also be obtained by alkylation of an organosilicon tertiary amine with agents such as methyl iodide or benzyl chloride. The pyridinium salts are readily prepared by the alkylation of pyridine with a halohydrocarbon-functional silane.

In the quaternary salt, X is an acid anion, for example, chloride, bromide or iodide anions; and carboxylate anions such as formate, acetate or trichloroacetate anions; and other acid anions, such as sulfate, sulfonate, phosphate and the like.

As described above, R can be any monovalent hydrocarbon radical of from 1 to 20 carbon atoms such as alkyl radicals,

alkenyl radicals, cycloaliphatic hydrocarbon radicals, aromatic radicals, aralkyl and alkaryl radicals. Because of the availability of such amines, it is preferred that the R substituents be alkyl groups. Other examples of monovalent hydrocarbon substituents attached to the nitrogen atom are well-known in the art and further listing of such substituents would be repetitious.

10 R', the linking group between the silicon atom and the nitrogen atom can be any divalent hydrocarbon radical containing from 1 to 18 inclusive carbon atoms such as $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-(\text{CH}_2)_3-$, $-(\text{CH}_2)_6-$, $-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}(\text{CH}_3)-$, $-\text{C}_{18}\text{H}_{38}-$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{C}_6\text{H}_5-\text{CH}_2-$, $-\text{C}_6\text{H}_4-\text{CH}_2-$, $-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2-$ and the like. Exemplary of the R' groups containing oxygen are those containing carbonyl groups, such as $-(\text{CH}_2)-\text{C}(=\text{O})\text{CH}_2\text{CH}_2-$, ether groups such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ and

$-\text{CH}_2\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{CH}_2\text{CH}_2-$, ester groups such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}(=\text{O})\text{CH}_2\text{CH}_2-$, $\text{CH}_2\text{OOCCH}(\text{CH}_3)\text{COO}(\text{CH}_2)_3$ and $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{CH}_2-$, hydroxyl-
20 containing groups, such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2-$, or a combination

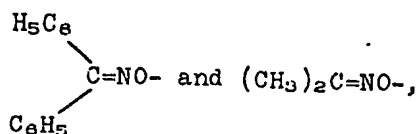
of such groups, such as $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2-$. R' can also

contain nitrogen in the form of $-\text{NR}''-$, for example, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2-$ or $-\text{C}_6\text{H}_5-\text{NCH}_2\text{CH}_2-$ wherein the R''

substituent on the nitrogen is a hydrogen atom or an alkyl radical of no more than 6 carbon atoms.

30 In addition to the hydroxyl group, the Y substituent on the silicon atom can be any hydrolyzable radical, such as

halogen atoms, hydrocarbonoxy groups, such as methoxy, acyloxy groups, ketoxime groups, for example,



and isocyanate group and certain configurations of trimethylsiloxy groups. As used herein, "hydrolyzable group" is defined as a silicon-bonded radical which reacts with water at substantially room temperature to form a silanol radical, i.e. $\text{≡SiY} + \text{HOH} \longrightarrow \text{≡SiOH} + \text{HY}$. Other than those described above, numerous other hydrolyzable groups are disclosed in the prior art.

Examples of organosilicon quaternary ammonium salts which can be used to coat solid fillers in accordance with the invention include $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$, $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)_2\text{C}_{18}\text{H}_{37}\text{Br}^-$, $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)_3\text{I}^-$, $(\text{C}_3\text{H}_7\text{O})_3\text{Si}-\text{C}_6\text{H}_4-\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)_2\text{CH}_2-\text{C}_6\text{H}_4-\text{Cl}^-$, $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{C}_{20}\text{H}_{41}\text{Cl}^-$, $\text{Cl}_3\text{Si}-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{Cl}^-$, $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{C}_{26}\text{H}_{57}\text{Br}^-$, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{C}_6\text{H}_4-\text{CH}_2\text{N}^+(\text{C}_6\text{H}_{17})_2\text{CH}=\text{CH}_2\text{Cl}^-$, $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2\text{Br}^-$, $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^+(\text{CH}_3)_2(\text{C}_{18}\text{H}_{37})\text{SO}_4^-$ and $(\text{CH}_3\text{CO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2-\text{N}^+(\text{C}_3\text{H}_7)_3\text{Br}^-$.

Because of availability and ease of synthesis, the salts preferred for use in the invention are those in which the acid anion (X) is chlorine or bromine; the divalent linking group (R') is a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2-$ group, and the hydrolyzable group (Y) is a methoxy or ethoxy

radical. It is also preferred that at least two of the R substituents on the nitrogen atom contain no more than 6 carbon atoms each.

The hydrolyzable groups such as chlorine atoms, methoxy and ethoxy radicals react with water either when added to an aqueous treatment media or when the treated filler is exposed to atmospheric moisture to form silanol groups which in turn condense to form a siloxane coating on the surface of the filler. The silanols will also condense with the silanol groups of siliceous surfaces to chemically bond or couple the siloxane to the surface. This chemical bonding is not a prerequisite to practice of the invention since the coating may also form an encapsulating surface about the solid.

The above-described quaternary ammonium organopolysiloxanes can be extended or diluted by incorporation of hydrocarbon or halohydrocarbon substituted siloxanes of the formula $R''' \frac{a}{2} SiO_{4-a}$ in which R''' is a monovalent hydrocarbon radical or monovalent halohydrocarbon radical and a has a value of from 0 to 1, thus in the manufacture of the salts the materials need not be purified. Such R''' substituents are described extensively in the literature. The incorporation of such siloxanes does not effect the cidal properties of the quaternary ammonium salts, thus the present invention is considered to include not only materials coated with the quaternary ammonium siloxane per se, but also solids coated with mixtures thereof and copolymers of such siloxanes with the described hydrocarbon and/or halohydrocarbon substituted siloxanes. For example, solids can be treated with an aqueous solution of a mixture of 0.5 mol of monomethyltrimethoxysilane or 3-chloropropyltrimethoxysilane and 1 mol of

$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^{\oplus}(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^{\ominus}$ to give an effective cidal coating. These coatings of the extended siloxane salt provide economy in the treatment of the filler.

The solid fillers to be incorporated in the polymeric matrix of the invention can be coated in any desired manner. A solvent solution of the siloxane can be applied to the solid by dipping or spraying and thereafter allowing the coated material to air dry or the coating step can be followed by heating. Preferably, the solid fillers are coated with an aqueous or organic solvent solution of the quaternary salts. Such solutions are easily prepared by adding the corresponding hydrolyzable silane to water or solvents, such as methanol, ethanol or hexane. It has been found that concentrations of from 0.25 to 10 percent by weight siloxane in the treating solution give satisfactory results. The treated surface is allowed to dry (or heated) causing a film of the siloxane to be coated on the surface of the solid. Heating the treated solid, say from 65 to 100°C. for a few minutes, will more firmly fix the siloxane coating on the surface. If desired, the conventional silanol condensation catalysts can be added to treating solutions to enhance the silanol condensation and provide improved bonding of the compounds.

The amount of organosilicon quaternary ammonium salt coated onto the solid is not narrowly critical so long as there is a sufficient amount that the desired type and level of cidal activity is present when the filler is incorporated in the polymeric matrix. In general, it has been found that fillers coated with solutions in the above concentration range, when dispersed in the matrix, effectively inhibit the growth of a variety of microorganisms. These

stated concentrations cannot be considered critical; obviously, the amount of filler present in the polymer and the degree of inhibition desired are factors determining the optimum concentration. Monomolecular layers of the siloxane salt have been found to be effective in several instances.

10 Fillers to be treated with the siloxane can be any type of non-water soluble solid including both inorganic and organic materials. The solids can be of synthetic or natural origin and include metals, metal oxides and carbonates, siliceous material, cellulosic materials, resins and plastics. Specific examples of suitable solids are metals and metal oxides such as iron, steel, aluminum, copper, nickel, titanium dioxide, alumina, zinc oxide, magnesium oxide, iron oxide, calcium carbonate and magnesium carbonate; siliceous materials such as glass, silica, diatomaceous earth, ground quartz, mica, asbestos, aluminum silicate, calcium aluminum silicate, magnesium silicate and zirconium silicate; resins and plastics such as polyester, polyamide, cellulose acetate, rayon, polystyrene, polyethylene, polypropylene, epoxy resins, phenolic resins, silicone resins
20 and polycarbonate resins; cellulosic materials such as wood, cotton and hemp and other naturally occurring organic materials such as silk and wool.

 The invention is directed to polymeric matrices having the coated filler dispersed therein, thus, the solid should be in a form suitable for dispersion, such as particulate or fibrous. The size of the particles or fibers is not critical, except that they must be capable of being dispersed in the matrix. Staple fibers, chopped strands and finely divided powders are preferred for use as the fillers.

Polymers in which the coated filler can be incorporated include naturally occurring polymers such as Hevea rubber and synthetic polymers, both thermoplastic and thermosetting. The term "polymer" is used in its generic sense and encompasses both homopolymers and copolymers. One class of polymers available for use in the invention are the vinylic polymers formed by the polymerization of aliphatically unsaturated carbon-carbon bonds such as those found in the vinyl group.

Exemplary of vinylic polymers are polyethylene, polypropylene, 10 poly(methacrylic acid), poly(acrylic acid), poly(ethylene-acrylic acid), poly(acrylonitrile-co-styrene-g-butadiene), polystyrene, polymethylmethacrylate, poly(methylmethacrylate-ethylmethacrylate), poly(acrylonitrilestyrene), polyisobutene, polyvinylchloride, polyvinylacetate, poly(vinylchloride-vinylidene chloride), poly(tetrafluoroethylene) and organic elastomers, such as natural rubber, ethylenepropylene terpolymers, polybutadiene, isoprene polychloroprene, styrene-butadiene rubber, butadiene-acrylonitrile rubber, poly(acrylonitrile)- 20 rubber and butyl rubber. Other vinyl polymers can be obtained from the polymerization or copolymerization of unsaturated amides, such as crotonamide, acrylamide and cinnamamide, unsaturated amines such as allylamine, allylethylamine and vinyl dimethylamine, unsaturated sulphides such as allyl sulphide and vinyl sulphide, unsaturated ketones such as methylvinylketone and allyl ketone and unsaturated isocyanates such as allyl isocyanate.

Other suitable polymers include condensation polymers such as polyester and alkyd resins which are obtained by the condensation of a polyhydric alcohol and a polycarboxylic acid.

30 Examples of polycarboxylic acid precursors to polyesters

include phthalic acid, phthalic anhydride, succinic acid, adipic acid, maleic acid, itaconic acid, isophthalic acid, terephthalic acid and the like. Polyhydric alcohols used in the preparation of polyesters and alkyds include glycols such as ethylene glycol, propylene glycol, diethylene glycol and dipropylene glycol. Polymers, such as the condensation products of bis-phenol and epichlorohydrin, epoxylated drying oils, the glycidol ethers of alcohols, epoxylated novolac resins, phenol-formaldehyde condensates, urea or melamine-formaldehyde condensates, polyurethanes, polysulfides, polyamides, polycarbonates, polyimides, organopolysiloxanes such as dimethylsiloxane rubber, phenylmethylsiloxane resins and 3,3,3-trifluoropropylmethylpolysiloxane and polyhydric polymers such as cellulose, starch and dextrin, can also be utilized as the polymeric matrix.

From the above listing of suitable polymers, it is apparent that the physical state of the matrix will range from that of a rigid solid to a flexible film to an elastomeric material to a gummy semi-solid to that of a thickened fluid or latex. The polymer can be cured or crosslinked or uncured depending upon the particular polymer and intended use of the article. If curing catalyst and/or crosslinking agents are used, they should not be reactive with the organosilicon quaternary ammonium compound to the extent that the siloxane coating is destroyed.

In addition to the coated filler, the polymeric matrix can contain other solid fillers and pigments as well as additives conventionally used with the particular polymer, such as plasticizers, oxidation inhibitors, lubricants, dyes, release agents and stabilizers.

The coated solid can be incorporated in and dispersed throughout the polymeric matrix in any convenient manner. If the polymer is liquid, such as uncured polyester resins, the siloxane-coated filler can be dispersed in the matrix by stirring. The filler can be incorporated in normally solid thermoplastic polymers such as polyethylene by mixing the solid with granules or pellets of the polymer and subjecting the mixture to heat and pressure while blending, such as takes place in an extrusion process. Elastomeric polymers and semi-solids can be
10 milled with filler to obtain dispersion throughout the matrix. Whichever method is used, it is preferred that the treated filler be uniformly dispersed throughout the polymeric matrix to avoid differences in physical properties within the matrix and to maintain a substantially constant level of tidal activity throughout the material.

The amount of coated filler incorporated into the composite article will vary but in all cases should be sufficient to provide that amount of organosilicon quaternary ammonium salt necessary to at least inhibit the growth of the
20 particular microorganism to which the article will be exposed, whether that microorganism be bacteria, fungi or algae. Thus, the optimum amount of filler added will depend upon the amount of organosilicon salt coated onto the solid, the level of activity of the specific organosilicon salt used to coat the filler, degree and type of inhibition desired, and the particular polymeric matrix. Filled polymers containing from about 5 to 150 parts by weight filler per 100 parts polymer are used in fabricating conventional composites and such a range of filler loading can be utilized in the practice of the present invention.
30 Generally, the incorporation of sufficient coated filler

to provide from about 0.05 to 5 weight percent, preferably 0.5 to 5 weight percent, of the organosilicon quaternary ammonium salt in the article (based on the weight of the polymer, coated filler, other fillers and additives) has been found to be effective in inhibiting the growth of a broad spectrum of bacteria, fungi and algae.

It is believed that cidal activity of the coated solid is available at the surface of the filled polymer and that inhibition results when the microorganism contacts the active solid. The organosilicon quaternary ammonium salt is not "applied to" the organism as is often the case when conventional antimicrobial agents are used, rather the microorganism is brought into "contact with" the salt.

It is apparent that articles fabricated from such filled polymers will find wide usage in providing protection from and control of destructive and pathogenic organisms. Standard fabrication techniques for the particular polymer can be used in making articles within the scope of the invention. Such techniques include casting, injection molding, profile extrusion, dip coating, impregnating fabrics and the like. Paint formulations having greater shelf life and yielding a dried paint film with increased resistance to fungal growth can be manufactured. Resinous binders and adhesives used in wood products can be formulated to prevent or minimize fungal discoloration and rot. Filled polymeric non-woven fabrics are useful as hospital garments and bandage wrappings. Elastomeric medical devices, such as catheters of natural or silicone rubber, are resistant to bacterial infection. By incorporating the coated filler in a waxy polymer, one can formulate polish compositions which act as disinfectants.

Fabrics impregnated or coated with a filled polymer find use in hospitals, restaurants, dairies, laundries and like environments where it is necessary to control and reduce bacterial activity. Pigmented polyester gel coats, such as used on the hulls of boats, are resistant to the growth of algae. From the foregoing description of useful articles, it is obvious that the invention contemplates articles formed only partially from the filled polymeric matrix, such as formed by coating such a material onto a substrate, as well as articles
 10 formed wholly from the described polymeric matrix, such as extruded profiles.

The following examples are illustrative and should not be construed as limiting of the invention delineated in the claims.

Example 1

Silica filler was treated with $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^{\oplus}(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^{\ominus}$ by adding 10 grams of a high surface area (240-270 $\text{m}^2/\text{gm}.$) finely divided fume silica to a solution of one gram of the organosilicon salt in
 20 125 ml. of hexane and the mixture was slurried. After one hour, the hexane was removed on a rotary evaporator at 90°C. The treated silica was then washed with 100 ml. of water and dried. The washed silica having a coating of $\text{O}_3/2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^{\oplus}(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^{\ominus}$ showed cidal activity (95% kill of S. faecalis).

The coated silica was milled with a standard silicone rubber gum to provide an elastomer stock containing 100 parts by weight of a dimethylvinyl-endblocked dimethylsiloxy-methylvinylsiloxy copolymeric gum, 40 parts by weight of the
 30 coated filler, 12 parts by weight of a dimethylpolysiloxane

fluid and about 2 parts of a peroxide curing catalyst. The rubber was molded into slabs and cured by heating. For purposes of comparison, another formulation containing the same ingredients, except untreated silica was used, was molded and cured in the same manner.

Three 0.25 x 1 inch samples were cut from each slab of cured rubber and then dipped in sterile saline solutions containing 30,000 E. coli B cells/ml. The inoculated samples were placed in sterile petri dishes on filter paper and incubated at 37°C. for 6 hours. The samples containing the coated filler showed no growth of the bacteria while the control samples (identical except that untreated silica was used) showed growth and colonization of E. coli B cells.

Example 2

The coated filler of Example 1 was incorporated in a standard silicone caulking composition which when cured exhibited antimicrobial activity. The caulking composition contained 140 grams of a hydroxy-terminated dimethylpolysiloxane high viscosity fluids, 2 to 3 grams of phenylmethylpolysiloxane, 9 grams of a monohydrocarbon triacetoxysilane (crosslinking agent) and 14 grams of silica filler. One particular formulation containing 10 grams of the coated silica and 4 grams of the untreated silica showed good antimicrobial activity when allowed to cure at room temperature. The caulk is especially useful for forming mildew-resistant seals around sinks and bathtubs.

Example 3

The effectiveness of the quaternary ammonium salt coating on silica in inhibiting the growth of algae was demonstrated by exposing various samples of styrene-butadiene

rubber to two strains of algae. A control samples of a filled styrene-butadiene rubber (the grade used in the sidewalls of tires) was cured at 150°C. for 30 minutes. A second sample of the same rubber was milled with sufficient $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+ (\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ to provide 1.5 weight percent of the quaternary ammonium compound in the sample which was molded into a slab and cured at 150°C. for 30 minutes. A third sample of the rubber was milled with a diatomaceous silica which had been teated to provide 10 weight percent coating of $\text{O}_3/2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+ (\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ on the particles. Sufficient treated silica was milled with the rubber to provide 1.5 weight percent of the siloxane in the rubber which was molded and cured in the same manner as the other samples.

Samples were cut into 3/4" by 1/2" pieces and placed in sterile petri dishes for exposure to algae. The samples were not washed prior to this testing and all samples were run in triplicate.

Stock cultures of Cyanophyta (a. blue-green algae), the Anabaena cylindrica strain, and Chlorophyta (green algae), the Selenastrum gracile strain, were each adjusted by dilution with sterile media to an algae cell count of 100,000 cells/ml. This adjustment was made using a counting chamber (haemocytometer) under a light microscope. A portion of the adjusted culture (0.1 ml.) was then placed directly on the surface of the rubber samples which were contained in sterile petri dishes. The inoculated samples were incubated for 30 minutes at $23 \pm 2^\circ\text{C}$. Following incubation, the samples were placed in individual test tubes containing 5 ml. of sterile algae growth media and shaken vigorously on a vortex mixer for 15 seconds. A portion of the supernatant was counted by light microscopy to determine

the decrease in viable cells as evidenced by rupture and loss of cell pigment. Results of testing with the different strains of algae are tabulated below:

Survival of *Anabaena Cylindrica*
on Rubber Surfaces

	<u>Sample No./</u> <u>Description</u>	<u>Avr. Cell</u> <u>Count/ml.</u>	<u>Survival</u>
	No. 1 - control with no quat salt	9450	94.5%
10	No. 2 - 1.5% quat salt added neat on mill	3000	30.0%
	No. 3 - 1.5% quat salt added as coating on silica	1100	11.0%

Survival of *Selenastrum Gracile*
on Rubber Surfaces

	<u>Sample No./</u> <u>Description</u>	<u>Avr. Cell</u> <u>Count/ml.</u>	<u>Survival</u>
20	No. 1 - control with no quat salt	9680	96.8%
	No. 2 - 1.5% quat salt added neat on mill	4420	44.2%
	No. 3 - 1.5% quat salt added as coating on silica	2175	21.7%

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These data demonstrate that the algacidal activity of the described quaternary ammonium salt is enhanced when the salt is present as coating on a solid filler. The siloxane coated filler was at least twice as effective as the same amount of quat salt which was incorporated as a neat fluid.

This same enhancement of activity was observed when the rubber samples were challenged with a mixture of fungi; namely, Aspergillus niger, Aspergillus flavus, Chaetomium globosum, Penicillium funiculosum and Aspergillus Versicolor.

10 Samples, in triplicate, were placed on agar plates and sprayed until wet with the fungal mixture. After 21 days incubation at 27°C., the control samples averaged 33% area covered with fungi, samples of the second rubber formulation (with quat salt added neat) averaged 26% area covered, while the samples containing the coated silica showed only 2% area coverage with the fungi.

Example 4

20 Finely divided diatomaceous silica having a surface area of about 4.5 m²/gram was treated with a 1% aqueous solution of $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}\text{Cl}^-$ by slurring about 500 grams of the silica with about four liters of the aqueous solution. After slurring, the silica was washed with water and filtered until the filtrate was free of chlorides. The treated washed silica was then dried at 100°C. for two hours to obtain a free-flowing material having about 0.75 weight percent of the siloxane salt coated onto the surface of the particles.

Pigment slip compositions containing 5, 10 and 20 weight percent of the treated silica (based on the weight of dry pigment) were formulated by blending titanium dioxide, 30 mica, calcium carbonate, aluminum silicate, the treated filler,

a surfactant, a glycol and a thickener in a blender until smooth dispersions were obtained. Portions of the dispersions were stirred with a commercially available acrylic latex (46% solids) to form acrylic paints containing 49 parts latex and 65 parts of pigment slip. Portions of the pigment slip were also blended with a commercially available polyvinylacetate latex (55% solids) to form a paint containing 41 parts latex and 65 parts of pigment.

Cedar wood panels were coated with the paint formulations (one panel per paint), allowed to air dry and then subjected to 100 hours in a weatherometer. The painted weathered panels were hung in a chamber that was maintained at 95% relative humidity and 29°C. The panels were positioned so as to allow air to freely circulate around the panels. Each panel was sprayed with a mixture of the following fungi: Aspergillus niger, Aspergillus flavus, Chaetomium globosum, Penicillium funiculosum, and Aspergillus versicolor. After a 14-day incubation period in the chamber, the extent of fungal growth was observed and recorded and the panels were resprayed with the fungal mixture. Following a second 14-day incubation period fungal growth on the panels was again recorded.

Results of this testing are tabulated below:

<u>Paint Formulation</u>	<u>Percent of Surface Coated With Fungal Growth</u>	
	<u>14 days after First Spraying</u>	<u>14 days after Second Spraying</u>
Polyvinylacetate Matrix with 0% treated silica	0	40
30 Polyvinylacetate Matrix with 5% treated silica in pigment	0	0

<u>Paint Formulation</u>	<u>Percent of Surface Coated with Fungal Growth</u>	
	<u>14 days after First Spraying</u>	<u>14 days after Second Spraying</u>
Polyvinylacetate Matrix with 10% treated silica in pigment	0	0
10 Polyvinylacetate Matrix with 20% treated silica in pigment	0	0
Acrylic Matrix with 0% treated silica in pigment	30	10
Acrylic Matrix with 5% treated silica in pigment	0	20
Acrylic Matrix with 10% treated silica in pigment	0	0
Acrylic Matrix with 20% treated silica in pigment	0	0

20 Although the polyvinylacetate paint exhibits initial resistance to fungal growth, when challenged a second time, substantial growth (40%) of fungi was experienced. The addition of a very small amount of the treated silica (5 weight percent silica containing about 0.75 weight percent siloxane salt in the pigment slip) to that polymeric matrix was sufficient to inhibit the growth of the fungi. This same observation can be made in the case of the acrylic paint formulation after the initial 14-day incubation period.

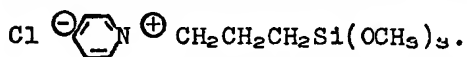
Example 5

30 The treated silica described in Example 3 was milled with natural rubber of the type utilized as tread

stock for heavy truck tires. Sufficient treated silica was added to give a rubber stock containing 1.5 weight percent of the quat salt coating. This rubber sample was molded into a slab and cured at 150°C. for 30 minutes. For purposes of comparison, the natural rubber (free of treated silica) was molded and cured in the same manner. Triplicate samples of both rubber formulations were challenged with the mixture of fungi and resistance to fungal growth was determined as described in Example 3. The control samples exhibited an average area covered of 21% while the samples containing the treated silica had only an average of 7% coverage.

Example 6

Three moles of pyridine and one mole of gamma-chloropropyltrimethoxysilane were reacted at 128°C. for 4 hours. Excess reactants were then removed under vacuum and the product was washed twice with ether to obtain the pyridinium quaternary salt of the formula



A solution of 0.55 grams of the above pyridinium salt in 10 ml. of methanol was mixed with 10 grams of high purity crystalline silica (10 micron size). After 30 minutes the methanol was removed under vacuum with a rotary evaporator to yield a silica containing 5 weight percent coating of $\text{Cl}^- \text{C}_5\text{H}_5\text{N}^+ \text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$ and $\text{Cl}^- \text{C}_5\text{H}_5\text{N}^+ \text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_2\text{O}$.

Five grams of the treated silica was blended with 16.8 grams of a solvated polyester resin (49.5% solids in xylol/butyl cellosolve - commercially available as Cargill 6603-60). The mixture was brushed onto Whatman filter paper and the filled polymer was cured at 95°C. for 18 hours. As

a control, a blend of 16.8 grams of the solvated resin and 5 grams of untreated 10 micron crystalline silica was also brushed onto Whatman filter paper and cured under the same conditions.

10 Triplicate samples (1/2-inch squares) of the cured polyester composites were placed in sterile petri dishes and sprayed with an aerosol of Escherichia coli B. The aerosol was prepared by adding 1 ml. of sterile water to 1 ml. of a culture of E. Coli B. which had been adjusted to an optical density of 300 at a wave length of 475. Following 30 minutes incubation of the samples at 37°C., the samples were placed in tubes containing 10 ml. of sterile nutrient broth and mixed thoroughly for 15 seconds. A 0.1 ml. sub-sample of each broth was then plated on nutrient agar. Colony counts were made on the agar plates after 24 hours incubation at 37°C. The resin samples containing treated filler exhibited an average colony count of 426 organisms as compared to an average of 582 organisms grown on samples containing the untreated filler. Thus, the article-prepared in accordance with the present invention gave a 27%
20 reduction in growth of the bacteria.

Example 7

Treated 10 micron silica samples containing 5 weight percent coatings of either $\text{Cl}^{\ominus}(\text{C}_2\text{H}_5)_3\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$ or $\text{I}^{\ominus}(\text{C}_2\text{H}_5)_3\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$ were prepared by the method described in Example 6. The treated silicas were incorporated in polyester resin and the resin composites cured and challenged with E. Coli B. utilizing the same methods and conditions as set forth in Example 6. The triethylchloride quat salt treated filler gave a 16.7% reduction in bacteria on
30 the resin composite (as compared to the control of Example 6)

while the triethyl iodide salt gave a 75% reduction in bacterial count.

Example 8

A waxy silicone polymer (stearyoxy-terminated polydimethylsiloxane) was blended with sufficient treated fume silica in a high shear mixer to provide 40 weight percent treated silica in the silicone wax. The fume silica had been treated with sufficient $\text{Cl}^{\ominus}\text{C}_{18}\text{H}_{37}(\text{CH}_3)_2\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ to provide a 10 weight percent coating of the corresponding siloxane.

- 10 The filled silicone wax was coated onto glass plates which were then inoculated with E. Coli B. and tested in the manner described in Example 6. For purposes of comparison, plates coated with just the silicone wax were also tested. The addition of sufficient filler to provide 4% of the quat. salt in the wax gave a 49% reduction in bacterial growth as compared to the control.

Example 9

- 20 Diatomaceous silica containing 0.75 weight percent $\text{Cl}^{\ominus}\text{C}_{18}\text{H}_{37}(\text{CH}_3)_2\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$ coating was blended with powdered polypropylene to formulate a thermoplastic molding compound containing 8 weight percent of the coated filler. The filled polypropylene was injection molded under the following conditions: front zone temperature - 246°C.; rear zone temperature - 221°C.; mold temperature - 49°C.; cycle time - 50 seconds and injection time - 7 seconds. A second sample of powdered polypropylene containing 24 weight percent of silica having 2.25 weight percent of the same quat salt coating was prepared and injection molded under the same conditions. For purposes of comparison, polypropylene molding
- 30 compounds containing 8 and 24 weight percent respectively of

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the same type of silica (but untreated) were also prepared and molded under the same conditions.

Three (1 x 3 cm.) pieces were cut from each of the above molded polypropylene samples and tested as follows: one piece was autoclaved at 120°C. for 15 minutes; one piece was autoclaved at 120°C. for 150 minutes and the last piece was not autoclaved and served as a control. All samples were placed on sabow and agar plates and sprayed with a spore suspension of the five fungi mentioned in Example 3. After 10 21 days of incubation at 25°C., the rate of fungal growth on the surfaces was determined by observing the number of foci of growth. Results are tabulated below:

<u>No.</u>	<u>Sample Description</u>	<u>Time Autoclaved at 120°C. (min.)</u>	<u>No. of Foci of Fungal Growth</u>
20	1 polypropylene with 8 wt. % of 0.75 wt. % quat salt treated filler	0	8
		15	11
		15	198
	2 polypropylene with 8 wt. % of untreated filler	0	19
		15	59
		150	298
	3 polypropylene with 24 wt. % of 2.25 wt. % quat salt treated filler	0	0
		15	1
		150	4
30	4 polypropylene with 24 wt. % untreated filler	0	13
		15	125
		150	207

These data demonstrate that polymeric matrices wherein only very small amounts of the quat salt coating are present, such as the .06 weight percent present in Sample No. 1, exhibit significant antimicrobial activity. Of course, at higher levels of quat salt coating the antimicrobial activity is greater. For example, Sample No. 3 contained 0.54 weight percent coating and exhibited only 3% area coverage after autoclaving for 150 minutes as compared to 100% area coverage for the control (Sample No. 4) which had been subjected to those same conditions.

10 Example 10

Titanium dioxide powder containing 10 weight percent $C_{18}H_{37}(CH_3)_2N^{\oplus}CH_2CH_2CH_2SiO_3/2$ was blended with polyamide (nylon 6-6) pellets in an amount sufficient to provide a nylon molding powder containing 0.75 weight percent of the siloxane coating. This material was injection molded at a temperature of 260°C. into a mold maintained at 55°C.; the cycle time being 50 seconds and injection time being 7 seconds. A second sample containing sufficient treated TiO_2 to provide 2.25 weight percent quat salt coating was formulated and molded under the same conditions. For purposes of comparison, unfilled nylon pellets were also molded under the same conditions.

Samples (3/4" x 1/2") were cut from each of the molded nylon composites. After being placed in sterile petri dishes, the samples were aerosol inoculated with 1 ml. of Streptococcus faecalis (1/10 dilution of an 18 hour broth culture) and 1 ml. of sterile water. The inoculated nylon surfaces were then incubated at 37°C. for 30 minutes. After incubation the nylon samples were placed in individual test tubes containing 10 ml. of sterile tryptic soy broth and shaken (vortexed) for 15 seconds. A 0.1 ml. subsample was

removed from each tube and plated on agar. Following incubation of the agar plates for 24 hours at 37°C., plate counts (number of bacterial colonies) were made. All tests were performed in triplicate.

Other portions of the nylon composites were subjected to the above-described procedure wherein Pseudomonas aeruginosa was used as the test organism. Again, all tests were performed in triplicate. Test results for both bacteria are reported below:

10

<u>Sample Description</u>	<u>Avr. Count</u> <u>X Bacterial/ml.</u>		<u>Survival</u>	
	<u>S.F.¹</u>	<u>P.A.²</u>	<u>S.F.¹</u>	<u>P.A.²</u>
Control - no treated filler	630	582	100	100
nylon with 7.5 wt. % TiO ₂ having 10 wt. % quat salt coating	168	205	26.7	35.2
nylon with 22.5 wt. % TiO ₂ having 10 wt. % quat salt coating	59	31	9.4	5.3

20

¹ - S.F. = Streptococcus Faecalis

² - P.A. = Pseudomonas aeruginosa

These data demonstrate the effectiveness of the organosilicon quaternary salt when coated onto a nonsiliceous solid.

Example 11

A 10 weight percent solution of
 $\text{Cl}^- \text{C}_{18}(\text{CH}_3)_2\text{N}^+ \text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ in isopropanol was added
 to an equivalent weight of glass beads. After mixing, the
 isopropanol was evaporated and the treated beads were oven

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dried at 90°C. for one hour to obtain glass beads containing 10 weight percent coating of $\text{Cl}^{\ominus}\text{C}_{18}\text{H}_{37}(\text{CH}_3)_2\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$.

The above procedure was repeated using $\text{Cl}^{\ominus}(\text{CH}_3)_3\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ to obtain glass beads coated with 10 weight percent $\text{Cl}^{\ominus}(\text{CH}_3)_3\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$.

The treated glass beads were mixed with the polyester resin described in Example 6 to produce composites containing 1.5 weight percent and 4.5 weight percent of the siloxane coating material. The composites were brushed onto Whatman filter paper and cured at 95°C. for 16 hours.

The cured composites were inoculated with E. Coli B. and subjected to the test procedure described in Example 6. The agar colony plate counts for the different samples are given below:

	<u>Sample Description</u>	<u>Count Bacteria/ml.</u>	<u>Survival of E. Coli B.</u>
	Control - no filler added	262	100
20	Polyester containing 15 wt. % filler having 10 wt. % coating of the trimethyl quat salt	0	0
	Polyester containing 45 wt. % filler having 10 wt. % coating of the trimethyl quat salt	2	0.8
	Polyester containing 15 wt. % filler having 10 wt. % coating of the octadecyl-dimethyl quat salt	60	23
30	Polyester containing 45 wt. % filler having 10 wt. % coating of the octadecyl-dimethyl quat salt	59	22.5

The activity of the trimethyl quat salt coating, $\text{Cl}^{\ominus}(\text{CH}_3)_3\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3/2$, is completely unexpected since the silane does not exhibit activity in solution, even when tested by the standard tube dilution method at one part per 100 against gram positive and gram negative bacteria.

Example 12

A solution of $\text{Cl}^{\ominus}\text{C}_{18}\text{H}_{37}\text{N}^{\oplus}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$ in toluene was slurried with fume silica for several hours. Toluene was then removed by filtration and the treated silica was washed with toluene and isopropanol until free of any unbonded silane. The silica containing about 10 weight percent of siloxane coating was oven dried. The treated silica was formulated into a topical base cream consisting of the following ingredients: 40.5 weight percent of mixture containing about 85% trimethyl-siloxy-terminated polydimethylsiloxane (350 cs.) and hydroxy-terminated polydimethylsiloxane and 15% of $\text{CH}_3\text{SiO}_3/2\text{SiO}_2$ copolymer; 12 weight percent of stearoxy-terminated polydimethylsiloxane (a waxy semisolid); 4.5 weight percent talc; 33 weight percent white petrolatum and 10 weight percent of the quat salt treated silica. The formulated base cream has the consistency of a tacky ointment.

When the above-described ointment was spread on a surface which was then challenged with Aspergillus versicolor, Aspergillus verrucaria, Aspergillus terreus and Penicillium funiculosum, the material gave complete inhibition of growth of the fungi, even after incubation at 25°C. for 48 hours.

Reasonable modification and variation are within the scope of the present invention which is directed to methods of inhibiting the growth of bacteria, fungi and algae in or on composite articles and composite articles exhibiting such antimicrobial activity.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of inhibiting the growth of bacteria, fungi or algae in or on a composite article having polymeric matrix comprising uniformly dispersing throughout the matrix a solid filler, said filler having coated on the surface thereof in an amount effective to inhibit such growth, an organosilicon compound selected from the group consisting of compounds of the unit formula $X^{\ominus}R_3N^{\oplus}R'\underset{\underset{\underset{Y_a}{|}}{\text{2}}}{SiO_{3-a}}$ and $X^{\ominus}\text{C}_6\text{H}_4N^{\oplus}R'\underset{\underset{\underset{Y_a}{|}}{\text{2}}}{SiO_{3-a}}$

in which X is an acid anion; R is a monovalent hydrocarbon radical containing from 1 to 20 inclusive carbon atoms, R' is a divalent hydrocarbon radical containing no more than 20 carbon atoms or a substituted divalent hydrocarbon radical of no more than 20 carbon atoms containing oxygen in the form of -COC-, $\begin{smallmatrix} \text{-COC-} \\ | \\ \text{O} \end{smallmatrix}$, $\begin{smallmatrix} \text{-C-} \\ | \\ \text{O} \end{smallmatrix}$, or $\begin{smallmatrix} \text{-COH} \\ | \\ \text{O} \end{smallmatrix}$ groups or nitrogen in the form of

RⁿN- groups in which Rⁿ is a hydrogen atom or a lower alkyl radical containing from 1 to 6 inclusive carbon atoms; Y is a hydroxyl group or a hydrolyzable radical; and a has a value of 0 or 1.

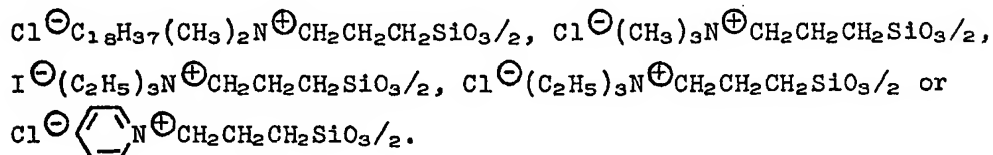
2. A method in accordance with claim 1 wherein in the organosilicon compound R is an alkyl radical.

3. A method in accordance with claim 2 wherein in the organosilicon compound at least two of the R substituents contain no more than 6 carbon atoms.

4. A method in accordance with claim 3 wherein in the organosilicon compound R' is a divalent hydrocarbon radical.

5. A method in accordance with claim 4 wherein in the organosilicon compound R' is a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ radical.

6. A method in accordance with claim 1 wherein the organosilicon compound is of the formula



7. A method in accordance with claim 1 wherein the coating of organosilicon compound is present in an amount in the range of from 0.05 to 5 weight percent based on the total weight of the composite article.

8. A method in accordance with claim 7 wherein said filler is present in an amount in the range of from 5 to 150 parts by weight per 100 parts by weight of polymeric matrix.

9. A method in accordance with claim 7 wherein the solid filler is a siliceous solid.

10. A method in accordance with claim 7 wherein the filler is silica or glass.

11. A composite article comprising a filled polymeric matrix having a solid filler dispersed uniformly therein, said filler having coated on the surface thereof an organosilicon compound selected from the group consisting of compounds of the unit formula $\text{X}^\ominus \text{R}_3\text{N}^\oplus \text{R}'\text{SiO}_{3-a} \underset{\text{Y}_a}{\frac{2}{2}}$ and $\text{X}^\ominus \text{C}_6\text{H}_5\text{N}^\oplus \text{R}'\text{SiO}_{3-a} \underset{\text{Y}_a}{\frac{2}{2}}$

in which X is an acid anion; R is a monovalent hydrocarbon radical containing from 1 to 20 inclusive carbon atoms, R' is a divalent hydrocarbon radical containing no more than 20 carbon atoms or a substituted divalent hydrocarbon radical of no more than 20 carbon atoms containing oxygen in the form of -COC- , -C(=O)- or -C(=O)OH groups or nitrogen in the form of R''N- groups

in which R'' is a hydrogen atom or a lower alkyl radical; Y is a hydroxyl group or a hydrolyzable radical; and a has a value of 0 or 1; said organosilicon coating being present in an amount sufficient to inhibit the growth of fungi, bacteria or algae in or on said composite.

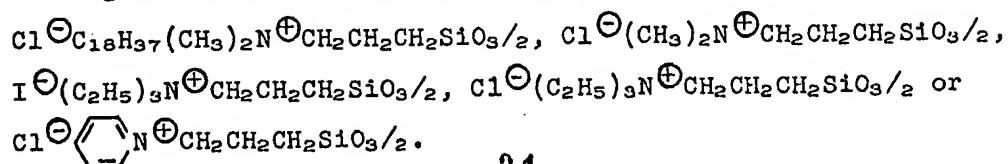
12. An article in accordance with claim 11 wherein in the organosilicon compound R is an alkyl substituent.

13. An article in accordance with claim 12 wherein in the organosilicon compound at least two of the R substituents contain no more than 6 carbon atoms.

14. An article in accordance with claim 12 wherein in the organosilicon compound R' is a divalent hydrocarbon radical.

15. An article in accordance with claim 14 wherein in the organosilicon compound R' is a $\text{-CH}_2\text{CH}_2\text{CH}_2\text{-}$ radical.

16. An article in accordance with claim 11 wherein the organosilicon compound is of the formula



17. An article in accordance with claim 11 wherein the coating of organosilicon compound is present in an amount in the range of from 0.05 to 5 weight percent based on the weight of the composite.

18. An article in accordance with claim 17 wherein said solid filler is present in an amount in the range of from 5 to 150 parts by weight per 100 parts by weight polymeric matrix.

19. An article in accordance with claim 17 wherein the filler is siliceous solid.

20. An article in accordance with claim 19 wherein the filler is silica.

21. An article in accordance with claim 17 wherein the filler is titanium dioxide.

22. An article in accordance with claim 17 wherein the polymeric matrix is a vinylic polymer.

23. An article in accordance with claim 22 wherein the vinylic polymer is polypropylene or a styrene-butadiene copolymer.

24. An article in accordance with claim 17 wherein the polymeric matrix is a condensation polymer.

25. An article in accordance with claim 24 wherein the condensation polymer is an organopolysiloxane, a polyester or a polyamide.



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Treatment of a solid filler with certain organosilicon quaternary ammonium salts and incorporation of the treated filler in a polymeric matrix imparts antimicrobial activity to the resulting composite article.